

# PATENT SPECIFICATION

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## (54) PROCESS FOR PREPARING 1,4-BUTANEDIOL

(71) We, MITSUBISHI PETRO-CHEMICAL CO. LTD., a Japanese Company of No. 3-1, 2-chome, Marunouchi, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for preparing 1,4-butanediol by reacting  $\gamma$ -butyrolactone with hydrogen using an improved copper oxide-chromium oxide catalyst.

It is known that 1,4-butanediol can be industrially prepared by the Reppe process in which 1,4-butyndiol, prepared by reacting acetylene with formaldehyde, is hydrogenated. It has also been known that dioles can be prepared by hydrogenating lactones using copper oxide-chromium oxide (copper-chromite) catalysts. However, the conventional copper oxide-chromium oxide catalysts used for that reaction rapidly lose their catalytic activity.

It has now been theorized that this loss in activity is a result of reduction of the copper component of the catalyst into metallic copper Cu. This conclusion is based on the findings of X-ray diffraction tests.

It would be desirable, therefore, to provide some techniques for inhibiting the formation of metallic copper by reduction, and thereby prolong the life of the catalyst.

The present invention, at least in its preferred forms can provide a process for preparing 1,4-butanediol in high yield by reacting  $\gamma$ -butyrolactone with hydrogen.

The invention, at least in its preferred forms, can also provide a process for preparing 1,4-butanediol in high yield and high selectivity by reacting  $\gamma$ -butyrolactone in the presence of an economically attractive catalyst.

According to the invention there is provided a process for preparing 1,4-butanediol by the reaction of  $\gamma$ -butyrolactone with hydrogen in the presence of a copper oxide-chromium oxide catalyst wherein the said copper oxide-chromium oxide catalyst con-

tains an additional component consisting of one or more of the following: a potassium compound, a sodium compound, a rubidium compound, an aluminium compound, a titanium compound, an iron compound, a cobalt compound and a nickel compound. Potassium, rubidium or iron compounds are preferred as the said additional components.

The specific catalyst used for the process of this invention may be prepared by mixing a compound of potassium, sodium, rubidium, aluminium, titanium, iron, cobalt, nickel or mixtures thereof into a conventional copper-chromium compound cake, as is used in preparing conventional copper oxide-chromium oxide catalysts. The copper compound-chromium compound cake (known as a copper-chromate cake) can be prepared by mixing a copper compound, such as cupric nitrate, with a chromium compound, such as ammonium chromate, with an aqueous basic solution, such as an ammonia solution. The particular manner of preparing the catalyst, however, is not critical. The copper oxide-chromium oxide catalyst is believed to be most active when the atomic ratio of Cu to Cr is approximately 1 for the  $\text{CuO} \cdot \text{CuCr}_2\text{O}_4$  component.

The additional component can be used in the form of a salt, particularly a nitrate or carbonate, which can be introduced into the cake in the form of an aqueous solution, if the metal component is other than titanium. If the additional component is a titanium compound, it may be used in the form of a paste for example a paste of titanium dioxide which has been prepared by kneading  $\text{TiO}_2$  with a small amount of water.

It is especially preferred that the additional component used be water soluble and be easily decomposed by heat to yield the corresponding metal oxide, without also yielding an undesirable residue i.e. a residue which adversely affect the activity of the catalyst. However, it is possible to use a water-insoluble component, such as titanium dioxide as stated above.

The copper chromate cake is mixed with the additional component and is then kneaded using an appropriate kneader. The resulting cake is dried at 100—110° C. and is decomposed by heat at 230—270° C., in air, and then is calcined at about 350° C. for about 1 hour to produce a copper oxide-chromium oxide catalyst. The calcination treatment can be conducted in an inert gas, such as nitrogen, but is preferably conducted in air.

The result of the calcination is that each of the metals present in the catalyst are in the form of their oxides.

The atomic ratio of the metal in the additional component to the copper in the copper component in the copper oxide-chromium oxide catalyst is preferably 0.005—0.2:1. When the additional component is a compound of potassium, sodium, rubidium, aluminum, titanium or iron, the atomic ratio may be 0.005—0.10:1, and is preferably 0.01—0.08:1. When the additional component is a compound of cobalt or nickel, the atomic ratio may be 0.05—0.20:1, and preferably 0.01—0.15:1. The additional component can alternatively be added to the copper oxide-chromium oxide catalyst by impregnating a solution of a compound of the additional component into the copper oxide-chromium oxide catalyst, and then calcining the mixture under suitable conditions.

This catalyst can then be used for hydrogenation of  $\gamma$ -butyrolactone usually within the temperature range of 150—260° C. and preferably 180—230° C. Below 180° C., the reaction velocity will be too low, and above 230° C., production of tetrahydrofuran, and n-butanol as byproducts will become too great.

The reaction velocity will, in general, be proportional to the reaction pressure. Good reaction velocities are attainable within the pressure range of 30 to 300 kg/cm<sup>2</sup>, and preferably 80—150 kg/cm<sup>2</sup>.

The catalyst can be used in the form of a powder suspended in a liquid phase, or it may be used in the form of particles in a fixed bed reactor, particularly if the reaction is con-

ducted in the vapor phase or in a vapor containing mixed phase.

Having now generally described the invention, a further understanding can be obtained by reference to certain specific Examples which are provided herein for purposes of illustration only and are not intended to be limiting in any manner.

#### EXAMPLE 1.

The catalyst was prepared by the following process:

An aqueous solution of 260 parts of cupric nitrate  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in 900 parts of deionized water was added dropwise to an aqueous solution of 151 parts of ammonium bichromate and 225 parts of a 28% ammonia solution in 900 parts of deionized water while stirring to yield a precipitate of copper-chromate. The temperature of the mixture was maintained at 75—85° C. while the components were being added. The precipitate was separated from the mother liquor by filtering to obtain 331 parts of a copper-chromate cake. According to the analysis, the copper compound is present in an amount of 13.0% by weight as Cu, and the chromium compound is 10.9% by weight as Cr, and the atomic ratio of Cu to Cr is 1:0.98.

An aqueous solution of potassium nitrate of  $\text{KNO}_3$  [0 g. (Catalyst-1), 0.063 g. (Catalyst-2), 0.159 g. (Catalyst-3), 0.317 g. (Catalyst-4), 0.475 g. (Catalyst-5), or 0.634 g. (Catalyst-6)] was added to 30 g. of the cake and the mixture was kneaded in a kneader and was dried at 100—105° C. After drying, the mixture was decomposed at 210—250° C. in an air flow of 500—700 cc./min. in a quartz tube having an inner diameter of 25 mm. and was calcined at 350° C. for 1 hour.

Into a 100 cc. autoclave, equipped with a magnetic stirrer, 40 g. of  $\gamma$ -butyrolactone was contacted with hydrogen at a reaction temperature of 200° C. under a reaction pressure of 100 kg/cm<sup>2</sup> in the presence of 1 g. of each catalyst prepared.

The results are shown in Table I.

TABLE 1

Catalyst	Atomic ratio of K/Cu	1,4-butanediol yield (wt. %)	Selectivity (wt. %)
1	0	44.4	99.5
2	0.01	51.8	99.0
3	0.025	60.5	99.4
4	0.05	51.3	99.2
5	0.075	44.9	99.5
6	0.10	32.6	99.7

Note: Catalyst-1 is a reference.

## EXAMPLE 2.

An aqueous solution of rubidium nitrate ( $\text{RbNO}_3$ ) [0.272 g. (Catalyst-7), 0.679 g. (Catalyst-8) or 0.905 g. (Catalyst-9)] was

added to 30 g. of a copper-chromate cake of Example 1, and each catalyst was prepared in accordance with the process of Example 1. The results are shown in Table II.

TABLE II

Catalyst	Atomic ratio of Rb/Cu	1,4-butanediol yield (wt. %)	Selectivity (wt. %)
7	0.03	51.0	99.5
8	0.075	58.9	99.7
9	0.10	43.2	99.6

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## EXAMPLE 3.

An aqueous solution of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) [0.163 g. (Catalyst-10), 0.325 g. (Catalyst-11), or 0.651 g. (Catalyst-12)] was added to 30 g. of the copper-chromate cake of

Example 1, and each catalyst was prepared in accordance with the process of Example 1, in the same condition.

The results are shown in Table III.

TABLE III

Catalyst	Atomic ratio of Na/Cu	1,4-butanediol yield (wt. %)	Selectivity (wt. %)
10	0.025	49.6	99.5
11	0.05	51.9	99.3
12	0.10	24.3	99.9

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## EXAMPLE 4.

An aqueous solution of aluminum nitrate  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  [0.58 g. (Catalyst-13), 1.15 g. (Catalyst-14), or 2.30 g. (Catalyst-25)] was added to 30 g. of the copper-chromate cake

of Example 1, and each catalyst was prepared in accordance with the process of Example 1, in the same condition.

The results are shown in Table IV.

TABLE IV

Catalyst	Atomic ratio of Al/Cu	1,4-butanediol yield (wt. %)	Selectivity (wt. %)
13	0.025	54.1	97.6
14	0.05	55.4	98.4
15	0.10	42.2	99.0

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## EXAMPLE 5.

A paste of the mixture of titanium oxide  $\text{TiO}_2$  [0.123 g. (Catalyst-16), 0.245 g. (Catalyst-17), or 0.490 g. (Catalyst-18)] and a de-ionized water was added to 30 g. of the cop-

per-chromate cake of Example 1, and each catalyst was prepared in accordance with the process of Example 1, in the same condition.

The results are shown in Table V.

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TABLE V

Catalyst	Atomic ratio of Ti/Cu	1,4-butanediol yield (wt. %)	Selectivity (wt. %)
16	0.025	51.8	98.0
17	0.05	51.4	98.0
18	0.10	43.4	99.2

## EXAMPLE 6.

5 An aqueous solution of nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) [0.446 g. (Catalyst-19), 0.892 g. (Catalyst-20), 1.339 g. (Catalyst-21), 2.14 g. (Catalyst-22) or 3.57 g. (Catalyst-23)]

was added to 30 g. of the copper-chromate cake of Example 1, and each catalyst was prepared in accordance with the process of Example 1, in the same condition.

The results are shown in Table VI.

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TABLE VI

Catalyst	Atomic ratio of Ni/Cu	1,4-butanediol yield (wt. %)	Selectivity (wt. %)
19	0.025	54.9	98.3
20	0.05	51.4	98.6
21	0.075	53.3	98.6
22	0.120	50.2	97.7
23	0.20	37.1	99.0

## EXAMPLE 7.

15 An aqueous solution of iron nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) [0.622 g. (Catalyst-24), 1.244 g. (Catalyst-25), 1.866 g. (Catalyst-26), or 3.732 g. (Catalyst-27) was added to 30 g.

of the copper-chromate cake of Example 1, and each catalyst was prepared in accordance with the process of Example 1, in the same condition.

The results are shown in Table VII.

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TABLE VII

Catalyst	Atomic ratio of Fe/Cu	1,4-butanediol yield (wt. %)	Selectivity (wt. %)
24	0.025	57.1	98.9
25	0.05	60.3	99.3
26	0.075	48.2	96.7
27	0.15	34.2	98.4

## EXAMPLE 8.

25 An aqueous solution of cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) [0.446 g. (Catalyst-28), 0.893 g. (Catalyst-29), 1.786 g. (Catalyst-30), or 2.679 g. (Catalyst-31)] was added to 30 g.

of the copper-chromate cake of Example 1, and each catalyst was prepared in accordance with the process of Example 1, in the same condition.

The results are shown in Table VIII.

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TABLE VIII

Catalyst	Atomic ratio of Co/Cu	1,4-butanediol yield (wt. %)	Selectivity (wt. %)
28	0.025	47.1	99.4
29	0.05	54.8	98.2
30	0.10	50.1	99.1
31	0.15	56.1	98.2

## EXAMPLE 9.

5 The copper oxide-chromium oxide catalyst in powder form containing potassium was tableted by a tablet manufacturing machine into a tablet 5 mm. in diameter and 5 mm. in height. Into a stainless steel reaction tube having an inner diameter of 28 mm. and 500 mm. in length, 30 cc. of the resulting catalyst

was filled and  $\gamma$ -butyrolactone was reacted at a reaction pressure of 100 kg/cm<sup>2</sup> and at a hydrogen velocity of 30 l/hr. (at the normal temperature and under the atmospheric pressure). 10

The yields and selectivities of the 1,4-butanediol at each duration of the reaction are shown in Table IX. 15

TABLE IX

Reaction duration (hr.) 1,4-butanediol yield (wt. %) Selectivity (wt. %)

1	73.1	99.3
4	87.0	99.1
8	81.3	98.7
12	86.7	99.2
16	86.8	99.1
20	90.6	99.2
22	90.2	99.1

20 Having now fully described the invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the scope of the invention.

## WHAT WE CLAIM IS:—

25 1. A process for preparing 1,4-butanediol by the reaction of  $\gamma$ -butyrolactone with hydrogen in the presence of a copper oxide-chromium oxide catalyst wherein the said copper oxide-chromium oxide catalyst contains an additional component consisting of one or 30 more of the following: a potassium compound, a sodium compound, a rubidium compound, an aluminium compound, a titanium compound, an iron compound, a cobalt compound and a nickel compound.

35 2. A process as claimed in claim 1, wherein the additional component is selected from an oxide of potassium, sodium, rubidium, aluminium, titanium, iron, cobalt or nickel or 40 a mixture of two or more of the said oxides.

3. A process as claimed in claim 1 or claim 2 wherein the atomic ratio of the metal of the additional component to the copper of the copper component of the copper oxide-chromium oxide catalyst is 0.005—0.2:1. 45

4. A process as claimed in any preceding claim wherein the hydrogenation of  $\gamma$ -butyrolactone is conducted at a temperature of 150—260° C.

5. A process as claimed in any preceding claim wherein the hydrogenation of  $\gamma$ -butyrolactone is conducted at a pressure of 30—300 kg/cm<sup>2</sup>. 50

6. A process as claimed in any preceding claim wherein said additional component is introduced into the catalyst in the form of a salt which is decomposed to form a corresponding oxide. 55

7. A process as claimed in claim 1 substantially as described herein with reference to the Examples. 60

8. 1,4-butanediol produced by a method as claimed in any preceding claim.

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R. G. C. JENKINS & CO.,  
Chartered Patent Agents,  
Chancery House,  
53/64 Chancery Lane,  
London WC2A 1QU.  
Agents for the Applicants.

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